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Injection moulding of hollow silicon nitride parts using fusible alloy cores

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Abstract

An interesting method of injection moulding originally developed for the plastic industry, is applied to technical ceramics in order to manufacture complex-shaped hollow parts at a reasonable cost. Silicon nitride parts are moulded on fusible alloy cores that are subsequently removed by melting before the final sintering step. Several parameters are investigated to remove the alloy cores without creating defects. Best results are obtained with a ceramic mixture based on a polyethylene binder phase and by melting the cores using an induction melting method. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Injection moulding; Fusible alloy core; Induction melting

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1. Introduction

In many industrial sectors, injection moulding is widely applied for the manufacturing of plastic and ceramic components [1]. The aim of the present work performed in the frame of the Brite/Euram Imhoco project (Injection Moulding of Hollow Components) is to develop an original processing method to manufacture hollow silicon nitride parts. Such parts, especially in the automotive industry, improve performances, getting significant advantages in part weight [2]. Pressurised gas was used in the plastic industry to produce hollow parts by injection moulding [3]. In this study, another route was chosen for manufacturing silicon nitride hollow parts by using a lost core technique : the ceramic feedstock is moulded on a fusible alloy core that is removed by melting before the final sintering step.

2. Materials

2.1. Ceramic powders (Table 1)

The silicon nitride powder used is the M11 grade from H. C. Starck. To fully densify silicon nitride during sintering, additives are needed to develop a liquid intergranular phase. Alumina (Baikowski CR 15 grade) and yttrium oxide Rhodia Terres Rares (Ceram 4N grade) allow us to obtain dense silicon nitride pieces with good mechanical properties [4].

2.2. Organic additives

Four types of organic additives are needed to manufacture parts by injection moulding : binders, plasticizers, dispersants and lubricants [5]. Binders give the necessary rheological behaviour to the feedstock for injection moulding and the cohesion to the green part. Plasticizers lower the viscosity of the binder to fit it to the process used. Dispersants improve the state of dispersion of the powder in the organic phase and prevent the formation of agglomerates. Finally, lubricants reduce wear between the feedstock and the tools. This organic phase has to wet the powder during mixing of

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Table 1
Powder characteristics

	Silicon nitride	Alumina	Yttrium oxide
Mean particle size (μm)	0.6	0.4	2
Specific surface area (m^2 g^{-1})	15	15	8.10
Purity	> 90% α-Si_3N_4	> 99% Al_2O_3	99.99% Y_2O_3

the feedstock, supply mechanical strength during moulding and debinding, and has to be fast and easily removed, with no residues which could alter material properties. One promising organic phase concept for injection moulding is the blend of waxes and polymers, as described below:

- back bone polymer, 9–39 wt.% of the organic phase, polar or non-polar, pure or blended polymer;
- waxes, 40–90 wt.% of the organic phase, one or more different melting points and different solubility in solvents;
- wetting agent, 1–21% of the organic phase (stearic acid, carnauba wax, esters).

Three different organic systems have been investigated during this work. They are listed in Table 2. Main differences arise in the choice of the backbone polymer nature and in the fraction introduced, thus allowing the modification of the viscosity and the stiffness of the organic phase. As a measure of stiffness, fracture energy and shore hardness from green parts have been determined. The fracture energy has been determined by a pendulum hammer at ambient temperature on moulded test pieces of a 7×7 mm^2 cross-section.

2.3. *Low fusible alloy*

Fusible alloys based on bismuth, tin and indium have low melting temperatures ranging from 80 to 200°C. Among them, we have chosen a Sn–Bi alloy with a melting point of 138°C supplied by Faci Europa (Italy). This alloy is easy to process. Its melting point allows moulding at usual temperatures and can be removed before the thermal elimination of the binder phase starts.

3. Forming of green ceramic samples (Fig. 1)

3.1. *Mixing step*

Mixing of the feedstock was performed in a 6 l Z-blade mixer (Aoustin, France) fitted with a rotating screw to extrudate and granulate the feedstock after mixing. Organic additives were first melted between 125 and 150°C (depending on the organic system) and the powder then slowly added. In order to increase the homogeneity of the powder distribution in the feedstock (especially the sintering additives), silicon nitride had been previously mixed with alumina and yttrium oxide (by ball milling in alcohol for 7 h). It is also possible to add the dispersant during the pre-mixing step to allow a better covering of the powder particles by the dispersant molecules. After drying, the powder was introduced into the melted organic phase. Mixing was performed for 4 h and the feedstock finally granulated.

3.2. *Rheological measurement*

The viscosity of the feedstocks was measured with a capillary rheometer (Göttfert, Rheotester 1000). The feedstock was introduced in a vertical heated cylinder fitted at its lower end with a round capillary (length: 20 mm, diameter: 1 mm). The feedstock was then forced through the capillary at controlled piston velocity and the pressure applied to the feedstock in the cylinder was recorded by a 0–100 MPa pressure transducer. The shear stress applied τ (Pa) was calculated from the recorded pressure. The shear rate $\dot{\gamma}$ (s^{-1}) was evaluated from the piston velocity and the capillary dimensions. Finally the viscosity η (Pa.s) was determined from the shear stress and the shear rate:

$$\tau = \eta.\dot{\gamma}^n \quad (1)$$

where n is the pseudoplasticity coefficient.

3.3. *Alloy cores manufacturing*

Alloy cores were obtained by a casting method. Alloys were first molten at 150°C and then cast in a preheated Teflon mould. The cast cores were then polished on both surfaces with SiC polishing plates until a smooth surface is obtained. Dimensions of cast alloy cores are given in Fig. 2.

Table 2
Binder systems used

Binder system	EVA-1	EVA-2	PE
Backbone polymer	Ethyl vinyl acetate (BASF, Germany)	EVA (BP Chemicals, France)	Linear high density polyethylene
Waxes	Paraffin types 50/52 and 62/64 from Bärlocher la Céresine (France)		
Carnauba wax	Carnauba type CT3 from Bärlocher la Céresine (France)		
Stearic acid	Supplier Merck, France		

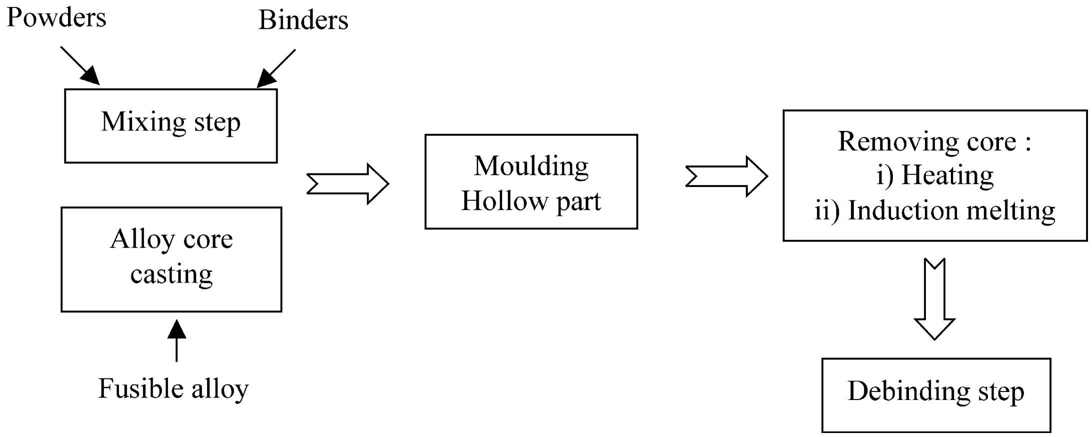

Fig. 1. Main steps of the forming process.

3.4. Injection moulding step

Samples were moulded on a high pressure injection moulding press [Arburg Allrounder 420C 1000 250 (Germany)]. Moulding of ceramic compositions needs to use specific injection screws with a low volume compression ratio (1.8 in the present case). Furthermore, the screw, the injection nozzle and the mould must be surface hardened in order to withstand abrasion caused by the ceramic particles. In this work, alloy cores were placed in the mould cavity against one face of the mould before moulding (Fig. 2). Dimensions of the core are such that it fits the cavity and no displacement occurs. Moulding conditions (pressure, temperature, cooling time) depend on the organic system used and are given in Section 4.2. After moulding, alloy cores were removed as detailed in Section 3. and the samples are debinded.

3.5. Debinding step

Moulded samples were first placed in a solvent (pentane, hexane...) at room temperature for a few hours. A fraction of the organic additives (about 30 wt.% of wax) was thus dissolved and removed from the samples. The remaining organics were then removed from the parts by thermal debinding. A low heating rate (0.5–1.5°C mn^{-1}) is necessary between room temperature and about 300 °C in order to avoid any cracks in the sample due to a high amount of gaseous products formed. A thermogravimetric analysis of the organic phase pyrolysis is useful to define the debinding cycle. In our case, debinding was performed up to 500°C preferably under inert atmosphere to avoid any oxidation of the silicon nitride powder.

4. Alloy cores removal

Two different techniques were investigated, (i) removal of the core by melting in a furnace during the first part of the thermal debinding step and, (ii) induction melting of the core just after the moulding step.

4.1. Melting in a furnace

Removal of the core by melting in a furnace is possible if the ceramic feedstock, on one hand, and the fusible

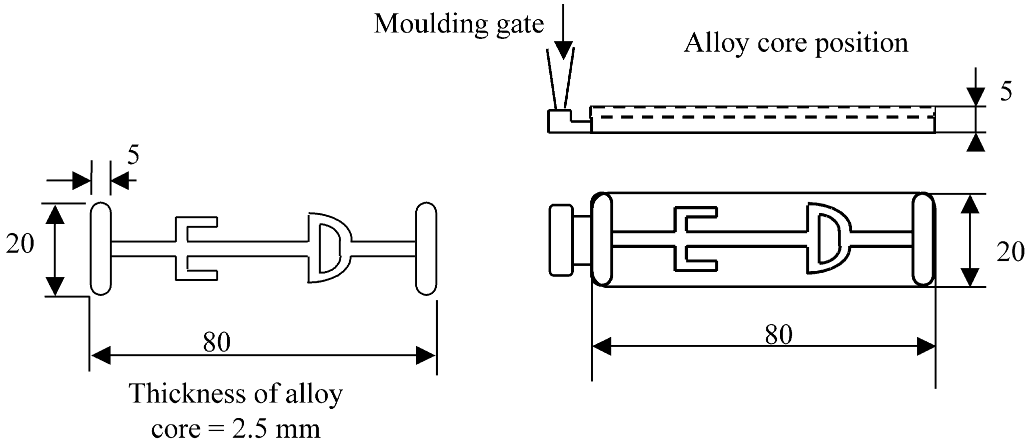

Fig. 2. Dimensions of the alloy core and of the moulded part.

alloy, on the other hand, have a similar dimensional behaviour during temperature variations. No significant loads should be applied to the green ceramic part to avoid cracks as it shows a brittle behaviour.

Dilatometric curves of the alloy cores and of the different feedstocks were determined between room temperature and their melting temperature. There is a large difference between the dimensional variation of the alloy core ($dL/L_{0}=1\times10^{-3}$) and that of the ceramic feedstock during cooling ($dL/L_{0}=1.25\times10^{-2}$). Shrinkage of the ceramic feedstock is due to the organic phase. This large mismatch may lead to crack formation during part cooling after moulding as the alloy core may prevent the ceramic feedstock to shrink safely. Probabilities of cracks or deformation to occur are thus high.

4.2. Induction melting

In order to lower the time needed to melt and to remove the core, the induction method has been investigated. The induction melting machine used had been provided by Celes (Lautenbach, France) (Fig. 3). The high frequency generator works in the 20–100 kHz range and is fitted with a potentiometer allowing to vary the induction power supply from 1 to 100% of full power (3 kW). The inductor itself is a horizontal cylinder (length: 200 mm, inner diameter: 35 mm) in which the moulded part is placed horizontally (with the core to be removed on the lower surface) just after the moulding step. It is supported by Teflon pins, above a Teflon container in which the melted alloy is recycled. It has been verified that a silicon nitride sample moulded without core does not heat at all when the magnetic field is applied.

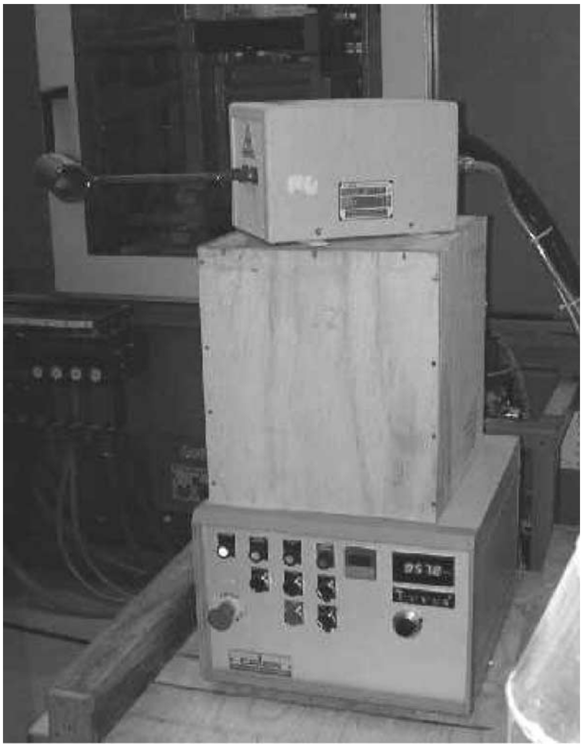

Fig. 3. Induction melting device provided by Celes (Lautenbach, France).

A rough calculation has been performed to estimate the time necessary to melt the alloy core using induction melting. The energy E required to melt the alloy part is given by:

$$E = m.C_{P}.\Delta T + m.H_{f} \tag{2}$$

where m is the core part weight (20 g), C_p the alloy specific heat (0.167 J g^{-1} K^{-1}), ΔT the temperature difference between the alloy melting point and room temperature (118 K), H_f the latent heat of fusion of the alloy (44.85 J g^{-1}). In our case, E is equal to 1291.12 J.

The theoretical time t (s) to melt the alloy is then equal to:

$$t = E/P \tag{3}$$

where $P(W)$ is the power delivered by the induction system. However, heating losses and real efficiency of the induction system have to be taken into account to determine the true melting time. With the system used, heating losses were estimated to average 30% of the energy delivered (70% were thus used to melt the alloy) and efficiency of the induction system was equal to 0.4 (it generally ranges between 0.2 and 0.8 depending on the optimisation of the inductor itself). Thus, time to melt the alloy is given by:

$$t = \frac{E}{0.28\ P} \tag{4}$$

As an example, if the power delivered by the induction system is equal to 1500 J s^{-1} (50% of full power), then only 3 s are necessary to melt the part of the alloy core submitted to the induced current located only in a skin just below the surface. Thus in fact, more time is necessary to melt all the alloy core. The induction melting device used works in the correct frequency range to allow melting the whole alloy core in less than 30 s at average power supply (1500 W) or in less than 3 minutes at low power supply (450 W). A short time is here beneficial to avoid the piece to cool down just after moulding and then to prevent from differential shrinkage.

5. Results and discussion

5.1. Feedstocks

Feedstocks with a 61% volume fraction of powder could be prepared with each binder system. Final compositions are given in Table 3. According to the rheolo-

Table 3
Compositions of the feedstocks

	Ceramic fraction	Binder	Remarks
Feedstock EVA-1	85.5 wt.%	EVA: 19 wt.% Paraffin wax: 69 wt.% Carnauba wax: 9 wt.% Stearic acid: 3 wt.%	EVA melting at 94°C, melt flow index: 3.9 g/10 mn
Feedstock EVA-2	85.5 wt.%	EVA : 33 wt.% Paraffin wax: 55 wt.% Carnauba wax: 9 wt.% Stearic acid: 3 wt.%	EVA melting at 97 °C, melt flow index: 1.2 g/10 mn
Feedstock PE	85.5 wt.%	PE : 30 wt.% Paraffin wax: 58 wt.% Carnauba wax: 9 wt.% Stearic acid: 3 wt.%	Linear high density polyethylene

gical behaviour (shear thinning behaviour), the mixing step used allows to obtain pastes free from agglomerates with a good state of dispersion. Especially powder agglomerates have a strong influence on defects formation in moulded samples [6] and have to be removed. The rheological behaviour of these mixes were determined at different temperatures in order to define the best moulding conditions. As shown in Fig. 4, the feedstocks have a shear-thinning behaviour which is suitable for high pressure moulding [7]. In the range of shear rates of high pressure injection moulding (i.e. 100–2500 s^{-1}), the viscosity of the feedstocks is located between 100 and 160 Pa s at 125°C for the EVA-1 system, between 100 and 220 Pa s for the EVA-2 system and between 100 and 280 at 150°C for the PE system. Differences in viscosity between the systems are in good agreement with the nature of backbone polymer used.

Measurements of fracture energy and of hardness of the different binder phases (performed to evaluate the influence of the backbone polymer) are given in Table 4. The change from EVA to the linear oriented polymer (PE) increases stiffness considerably. The shore hardness values (shore D, sharp tip) does not show such a pronounced effect of the polymer on the property (Table 4). Hardness does not react so severely on the chain structure of the polymers. As both polymers, EVA and linear PE, are basically the same polymer type, this result is obvious.

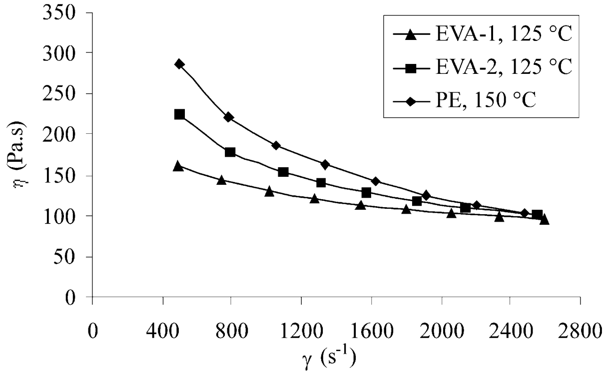

Fig. 4. Rheological behaviour of the feedstocks.

5.2. *Injection moulding and debinding of samples without alloy cores*

In the case of the EVA binder systems, samples were injection moulded with a screw and nozzle temperature of 125°C, a mould temperature of 60°C, an injection rate of 30 cm^3 s^{-1}, a 100 MPa injection pressure and a cooling time of 15 s. Using the PE system, parts were moulded at 150°C in a mould heated at 65°C, the other parameters being the same. Defect-free samples were obtained after debinding. The injection and thermal debinding process thus allows to obtain an uniform microstructure before sintering. The green density appears suitable (~60%) in order to achieve 100% dense samples after sintering.

5.3. *Moulding of samples with alloy cores: removal of cores by melting in a furnace*

As the injection temperature of the PE system is equal to 150°C (thus higher than the alloy melting point), we first verified that the alloy core does not start to melt during moulding when the feedstock enters the mould, providing the core is placed cold in the mould just before the moulding shot.

Table 4
Fracture energy and hardness values of the different feedstocks

Green part feedstock	Fracture energy (J cm^{-2})	Hardness (shore D)
EVA-1	0.72	61
PE 30%	1.09	65

Whatever the organic system used, parts moulded with alloy cores and allowed to cool down at room temperature crack and bend (Fig. 5). This is due to the high mismatch between the dimensional variations of the green ceramic part and of the fusible alloy during cooling as discussed in Section 3.1. Even the increase in stiffness of the PE binder (30% increase compared to the EVA binder) does not allow the moulded part to withstand stresses developed in the ceramic-binder phase during cooling. If the parts are immediately loaded in the furnace after the moulding step, the necessary time to melt the alloy is too long (>15 min) and the ceramic part softens and collapses before a significant part of the core is removed.

5.4. Moulding of samples with alloy cores: removal of cores by induction melting

5.4.1. Parts moulded with the EVA binder systems

Removal of the alloy core by induction melting leads to part deformation with the EVA binder systems (Fig. 6). At average induction power supply (1500 W), the alloy core is melted within 30 s and a major fraction is removed from the part. However, the heat developed in the core is high and leads to the softening of the organic phase by heat conduction (the temperature reached in the ceramic part is above 90°C). Thus, the part collapses. Even at low induction power supply (450 W), the binder phase softens and the part starts to deform before the alloy has been removed. As a conclusion, the EVA binder type is not suitable for removal of the core by induction melting. The binder viscosity becomes too low and the part collapses during induction melting due to the temperature increase in the ceramic-polymer phase by heat conduction.

5.4.2. Parts moulded with the PE binder system

Removal of the alloy core by induction melting at low inductor power supply (450 W) can be performed without part deformation, providing the part is well supported. A major fraction of the core is molten and removed from the part in 3 min (Fig. 7). In this case, the temperature increase within the green ceramic part by heat conduction still softens the organic phase but the higher melting point and the higher viscosity of the PE binder (compared to the EVA-binder) prevent the part from collapsing during induction melting.

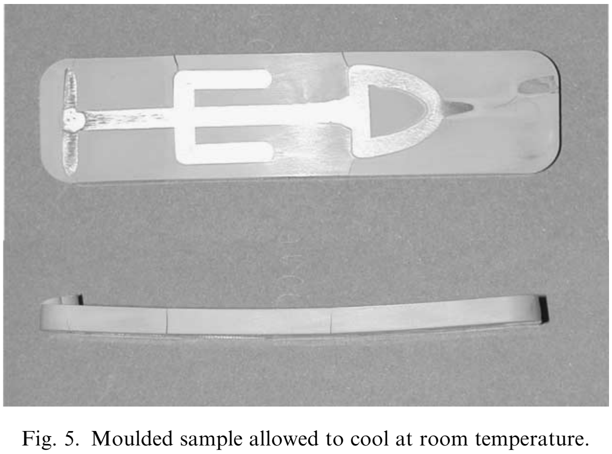

Fig. 5. Moulded sample allowed to cool at room temperature.

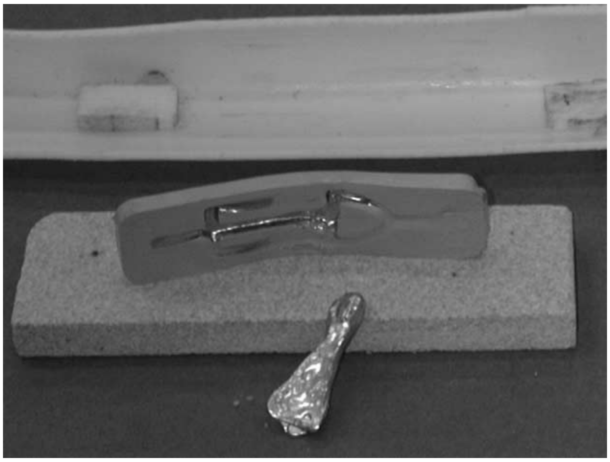

Fig. 6. Removal of the core by induction melting from a sample moulded with EVA-2 binder.

Some samples have been satisfactorily further debinded after the induction melting step. But, after debinding, some alloy remains in the sample.

As a conclusion, removal of alloy cores by induction melting is possible when using a high melting temperature and a high viscosity polyethylene based binder phase which is able to sustain the temperature increase due to heat conduction. Furthermore, the induction power supply should be low in order to prevent overheating of the green ceramic part during induction melting. Finally, some alloy still remains in the parts after induction melting and debinding. Thus, to perform successful debinding, the core geometry must be well defined, the shape of the cores has to be as round as possible and the core surface has to be very smooth to facilitate the alloy flow during the core removal. Fur-

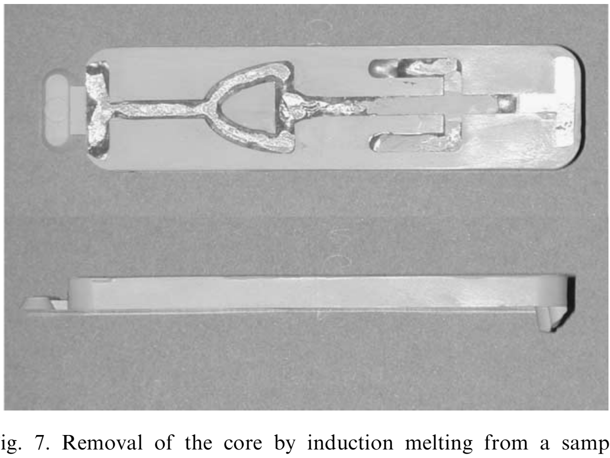

Fig. 7. Removal of the core by induction melting from a sample moulded with PE binder.

thermore, the core design should minimise stress raising edges with respect to moulded material around the core. Finally, alloy traces that remain after debinding can be removed from the part by immersion in a glycol based solvent.

6. Conclusions

A new method has been investigated in order to manufacture complex ceramic hollow parts at a competitive cost. Ceramic parts have been obtained by high pressure injection moulding on low fusible alloy cores that are removed by melting after the moulding step. Different feedstocks and core removal techniques have been studied. Best results were obtained with a feedstock based on a high density polyethylene binder phase and by removing the core by induction melting immediately after part ejection from the mould.

Main parameters governing this process are the viscosity of the binder phase which should be high enough to avoid collapsing of the part during removal of the core, and the core surface which should be very smooth to allow a good flow of the alloy from the part during induction melting. Polyethylene binder allows us to mould parts with moulding conditions that avoid core deformation, and gives sufficient yield strength to the moulded part during core removal. Surfaces of the core were polished but one can imagine to manufacture cores with a good surface, finish by injection moulding or pressure casting is needed.

The next step to fully develop this manufacturing process is now to remove alloy traces that can remain on the ceramic part after the induction melting step and to define the best sintering cycle.

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References

[1] B.C. Mutsuddy, R.G. Ford, Ceramic Injection Moulding, Chapman and Hall, 1995.
[2] F.L. Riley, 2nd European Symposium on Engineering Ceramics, Elsevier Applied Sciences, Amsterdam, 1987.
[3] L. Johnson, P. Olley, P.D. Coates, Gas assisted injection moulding: finite element modelling and experimental validation, Plastics, Rubber and Composites 29 (1) (2000) 31–37.
[4] E.Y. Sun, P.F. Becher, et al., Microstructural design of silicon nitride with improved fracture toughness: II, effects of yttria and alumina additives, J. Am. Ceram. Soc. 81 (11) (1998) 2831–2840.
[5] R.M. German, Powder injection moulding, MPIF, Princeton, 1990.
[6] D.M. Liu, W.J. Tseng, Influence of powder agglomerates on the structure and rheological behavior of injection-molded zirconia-wax suspensions, J. Am. Ceram. Soc. 82 (10) (1999) 2647–2652.
[7] D.M. Liu, W.J. Tseng, Rheology of injection-molded zirconia-wax mixtures, J. Mater. Sci. 35 (4) (2000) 1009–1016.